

The Osmotic Pressure of Cane
Sugar Solutions at 0°.

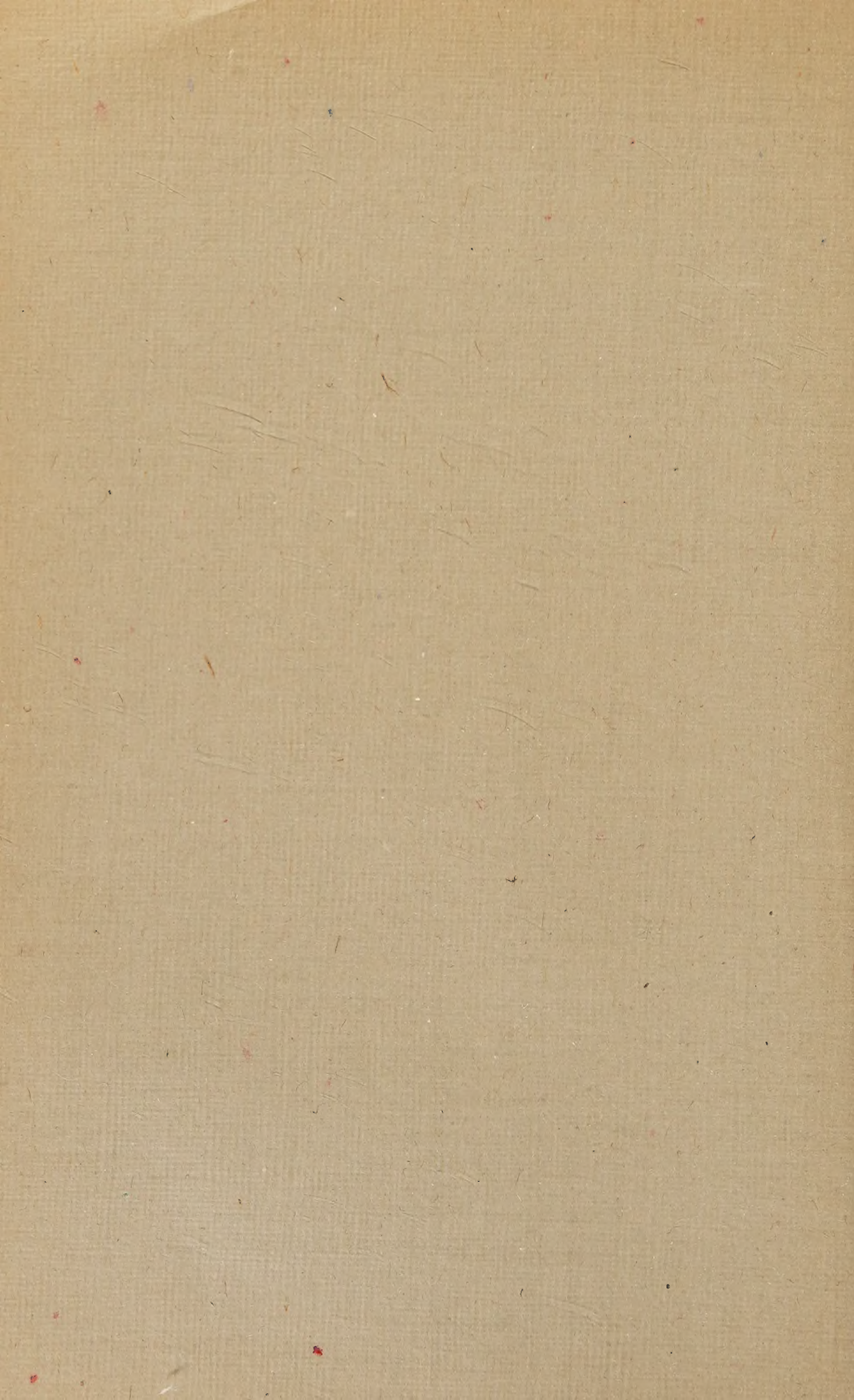
DISSERTATION

SUBMITTED TO THE BOARD OF GRADUATE STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.

BY

EMANUEL G. ZIES.

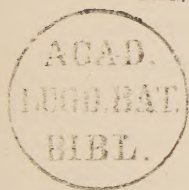
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CONTENTS.

	Page
Acknowledgment	4
Introduction	5
Discussion of Previous Work at 0°:	
Dilution and Thermometer Effects.....	6
Inconstancy of the Temperatures.....	6
The Osmotic Pressure of Cane Sugar Solution at 0°:	
Temperature Control.....	7
The Cells.....	10
Experimental Part	11
Summary of Results.....	24
Discussion of Results.....	25
Barometer Effect.....	26
Table of Comparative Accuracy.....	29
Temperature Coefficient.....	30
Biography	32

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The author desires to take advantage of this opportunity to express his gratitude to President Remsen, Professor Morse, Professor Jones, Professor Renouf, Professor Matthews, and Associate Professor Acree for instruction in the laboratory and lecture room.

This investigation was pursued under the supervision of Professor Morse, to whom the author is especially indebted for valuable assistance and many suggestions.

THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 0°.¹

Introduction.

Ever since the time Van't Hoff² brought out the importance of Pfeffer's³ work on the osmotic pressure of solutions, much interest has been shown in all subsequent work on the same problem, for it is believed that a clearer insight into the nature of osmotic pressure will give a better insight into the nature of solutions. The difficulties, however, which beset the path of all who attempt to study osmotic pressure have been so great as to discourage the most earnest worker from making any further attempts along this line. In this laboratory much work has been done on this problem by Professor Morse and his co-workers; many years have been spent in preparing the proper kind of cell, the proper kind of membranes, and in preliminary measurements with such cells and membranes. Difficulty after difficulty has been overcome until the measurement of osmotic pressures has reached such a stage that the determination of the temperature coefficient of osmotic pressure can be made. Having brought the work to this degree of accuracy, it

¹ The author desires to express his appreciation of the kind assistance rendered by Mr. Gentry Cash.

² *Zeit. für Phys. Chem.*, 1, 481 (1887).

³ *Osmotische Untersuchungen* (1877).

was thought desirable to repeat the previous determinations of the osmotic pressure of weight normal cane sugar solutions at 0° and other higher temperatures in order to find if the law of Gay Lussac holds.

The previous work at 0° was greatly beset with the difficulties of dilution¹ and thermometer effects;² the nature of these difficulties has been fully described on several occasions and need not be repeated here. When the present work was begun the trouble caused by dilution had been overcome, thus doing away with corrections of uncertain value, but the thermometer effects were still a source of much trouble. At the higher temperatures the thermometer effects had been overcome by the construction of a bath in which practically constant temperatures could be maintained for any required length of time. It is obvious that at 0° , unless resort is had to very expensive mechanical refrigeration, no such system³ of alternately heating and cooling of the bath as devised for the higher temperatures could be used.

A perusal of the previous⁴ work at 0° will show first, that 0° never was reached; secondly, that the temperatures for any one experiment never were constant, the extreme variation being from $0^{\circ}.12$ to $0^{\circ}.38$, the average variation from $0^{\circ}.15$ to $0^{\circ}.30$; and thirdly, the temperature of the solution was greatly dependent on the temperature outside of the bath. The temperature of the air space above the water in which pressure apparatus was immersed showed even greater variations. Since the manometers extend up into this air space, its temperature is supposed to be that of the nitrogen in the manometers. Variations in the temperature of the air space are, however, not of as serious a nature as variations in temperature of the solution whose osmotic pressure is to be determined, in as much as, the expansion of the solution in the cell, caused by rising temperature, is much more rapid than flow of water out of the cell, hence the pressures are abnormally

1 Am. Chem. J., 36, 26 and 49; 37, 328, 427, 463, 559 and 582.

2 Ibid, 34, 24.

3 Ibid, 47, Feb., 1909.

4 Ibid, 37, May 1907.

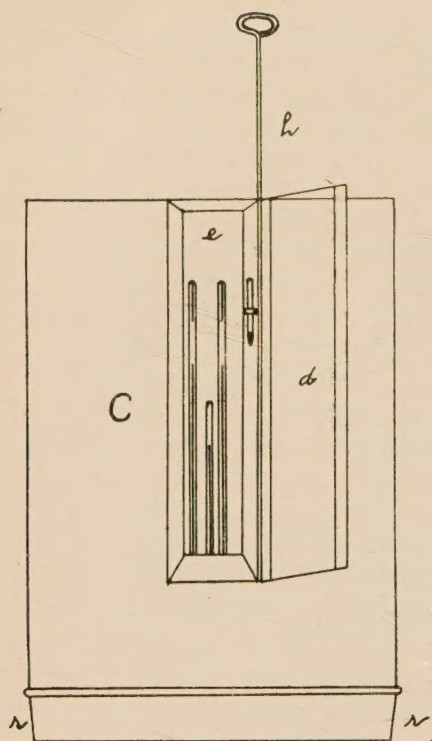


FIG. 1.

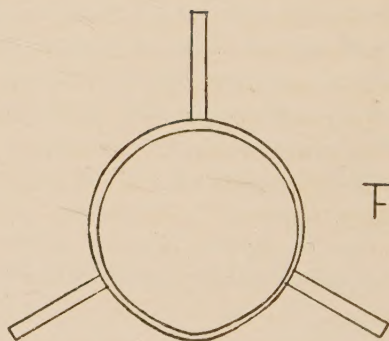
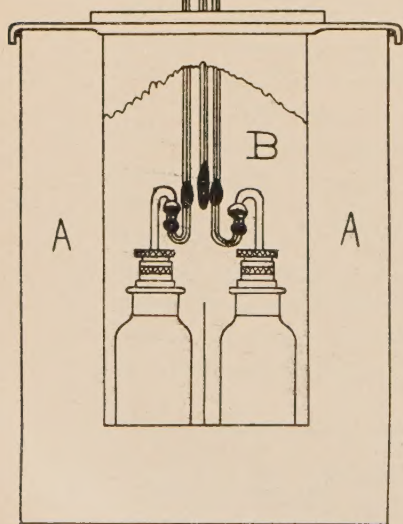


FIG. 2.

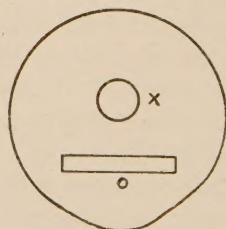


FIG. 3.

large and several hours must elapse before readjustment of osmotic pressure and rise in temperature is brought about. In the meantime, however, another change in temperature may take place, thus bringing about a new state of affairs before the old has been properly adjusted. With these difficulties in mind, it was thought desirable to try a different method for obtaining a constant temperature in the vicinity of the freezing point of water. In the former method, the attempt was made to cool off the water in the bath by immersing in it perforated cans filled with ice and providing for a rapid circulation of the water around the ice. Since the method of determining the zero point on a thermometer, namely, to surround the bulb with pure melting ice, is an effective one, it seemed that this same plan could be adopted in maintaining 0° in our solutions. With this idea in mind the following ice bath was devised.

Temperature Control at 0° .

The bath as used for the higher temperatures has been fully described elsewhere¹ and is known in this dissertation as the main bath. All the water was removed from the main bath and all the mechanical contrivances for circulating the water were taken out. A circular galvanized iron can 41 cm. in diameter and 50 cm. high was placed in the bath. The can was perforated at the bottom and when in position was raised from bottom of main bath by about 10 cm. This can is indicated by the letter A in the illustration opposite. Within was placed a smaller can, B, which was suspended in centre of outer can by the saddle shown in Fig. 2. The space between the two cans was firmly packed with finely crushed ice. This inner can was large enough to hold two pressure measuring outfits. This outfit consists of a bottle holding the water in which the cell and its attached manometer are placed. On placing this measuring apparatus in position, can B is covered with the cap shown in Fig. 3. This cap fits B somewhat loosely, thus allowing for adjustment of the manometers

(1) Am. Chem. J., 36, 1-12.

which pass through the opening in cap designated by, o. In addition the cap is provided with an opening, x, to permit the insertion of a thermometer for ascertaining the temperature of B.

After the cap has been placed in position, any open spaces which may remain around the manometer stems where they pass through the cap are closed with wads of raw cotton. The cylinder designated by C in Fig. 1 is now placed over can A and is held in position by the offset, r, which fits inside of can A. This upper section or cylinder C is provided with a recess, e, which permits the observation of the thermometer and of the manometer stems which come through the cap just described. This recess being open only at the bottom, protects the manometers from the ice with which section C is now filled. In order to obtain the temperature of the nitrogen in the manometers, a thermometer, t, is placed in the upper portion of the recess. This little observation chamber, as it may be called, is closed by the padded door, d, which can be opened or closed by means of the handle, h, from the outside of the main bath.

This handle passes through the top of main bath and is in two sections, allowing the upper part to be removed when main bath is opened. The space between the can A, together with its upper section and the main bath, is filled with crushed ice, which acts as a most effective insulation for can A. The water which accumulates on the bottom of the bath is drained off by an automatic syphon, which never allows the water to reach the bottom of can A.

As was stated before, can A was raised from floor to main bath, and in addition was perforated at the bottom. This allows the water resulting from the melting of the ice to drain off, and thus it never accumulates. The result is that the inside of B is always at the same temperature, namely, that of the melting ice. It is evident that the inner can B, save for the small area taken up by the recess, is completely surrounded by finely crushed melting ice. In addition the ice in A is prevented from melting away too rapidly by the protective insulation of ice surrounding it in the main bath; finally, the

main bath itself is well insulated. This may seem like an enormous waste of ice and it is true that it required 300 kilograms of ice to fill the bath, but the quantity of ice which had to be added from day to day in order to keep the the original amount constant amounted to only 20 to 25 kilograms.

In order to take measurements, the felt pads which cover the plate glass windows of the main bath were removed and the door closing the recess was then opened, the temperature of the inside of can B and of the recess were read and by means of the cathetometer the measurement of the nitrogen volume was made in the usual way. During the time that the reading was made the temperature of the air space rose at times as much as $0^{\circ}.5$, but this final temperature was not taken into account, since, owing to the thickness of the glass walls of the manometer stem, this change in temperature does not influence the nitrogen volume within the short time taken up by the observation.

This question of temperature leads to a discussion of the temperatures obtained in the can B, and in the recess, *e.* Throughout this work the temperature of B is recorded as the temperature of the solution in the cells and the temperature of the recess as that of the nitrogen in manometers. The zero points on both thermometers were carefully determined, independently, by three observers. On examining the records of the measurements tabulated in this dissertation it will be seen that the temperature of the solution in every experiment never varied sensibly from 0° . The temperature of the nitrogen in the manometers, on the other hand, varied between $0^{\circ}.0$ and $0^{\circ}.5$, being dependent to a certain extent on outside temperature conditions, but never varied as much as in previous work in the vicinity of $0^{\circ}.0$. The temperature of the solution seemed to be independent of external conditions, for, although the temperature of the atmosphere for several days was as high as 29° , yet the space B, in which the cells were located, did not deviate sensibly from $0^{\circ}.0$. When the bath was repacked with ice for the purpose of making measurements of osmotic pressure the space B was ordinarily $0^{\circ}.1$

above $0^{\circ}.0$, but after completion of the operation of packing the temperature slowly sank to $0^{\circ}.0$ and remained at this point without sensible variation to the end of the experiment. In view of the constancy of the temperature which was maintained throughout the work it is believed that these results were very slightly, if at all, influenced by thermometer effects.

On completing an experiment the ice was taken out of section C, which was then removed from can A, thus allowing the removal of the cells from B. Before starting another experiment the ice was repacked firmly in and around A and the remainder of the operation carried out as described above.

The Cells.

The cells which were used in these measurements were the same as those devised by Morse and Mears¹; the manner in which the cells were closed has been of enormous help in eliminating all errors due to dilution. Formerly, this operation required almost an hour, thus exposing the cell to many sources of error; now, after the cell has once been filled, it can be closed, or after a measurement it can be opened in about half a minute. This shortening of the time required for closing and opening the cells has added greatly to the precision of the measurement of osmotic pressure. Formerly, on account of the considerable length of time required for these operations there was an unavoidable sucking in of water from cell wall, which resulted in more or less serious dilution of the solution. As has been said before¹ if all this dilution occurred while cell was being set up it would not be a matter of great importance, or if it occurred exclusively at the opening of the cell it would likewise be unimportant; for, in the first case, the pressure could be corrected for the whole of the dilution as measured by the polariscope; in the second case, it could be neglected as having occurred subsequent to the measurement of pressure. It was impossible to ascertain how much of the

(1) Am. Chem. J. 40, 226-267.

(1) Am. Chem. J., 36, 26, 49; 37, 589.

total dilution occurred while setting the cell up and how much while it was being opened.

Previous to setting up a cell for a measurement, fresh membrane was electrically deposited in the cell at a temperature close to that at which the cell was to be used for a measurement. In this work at $0^{\circ}.0$ the membranes were deposited at a temperature of about $0^{\circ}.2$. The resistance offered to the passage of the electrical current by the membrane increased markedly at this temperature; it seemed as though the membrane became denser and stronger. As a matter of fact several cells which had proven almost worthless at higher temperatures were developed into good cells in the course of the work at $0^{\circ}.0$. Then, too, whether in use or out of use, the cells were always maintained as close to $0^{\circ}.0$ as possible, and whenever a cell was set up for a measurement the solution inside and the water on the outside of cell were previously cooled down to $0^{\circ}.0$.

Experimental Part.

Heretofore the cane sugar, which was used for osmotic pressure determinations, was obtained in Baltimore in the form of "rock candy" and was usually pure enough for immediate use. This year, however, the various samples of "rock candy" which were tested as to their purity contained a larger amount of invert sugar than that used in previous years; hence all the sugar had to be purified. The method of purification which was used was a modified form of the method described by Cohen and Commelin¹. The sugar was precipitated by ethyl alcohol, washed first with ethyl and then with methyl alcohol. Thereupon it was carefully dried at 60° in an air bath and, finally, in a vacuum desiccator over calcium chloride.

The results obtained by means of the apparatus and sugar above described have been tabulated on the following pages in the usual manner, the essential data of each experiment being recorded. All pressures are recorded in atmospheres.

(1) Zt. Phys. Chem., 64, 1.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 12.65; (2) at conclusion of expr., 12.65; loss, 0=0 per cent. *Manometer*: No. 13; volume of nitrogen, 263.04. Cell used, K_8 . Resistance of membrane, 545,000. *Corrections*: (1) liquids in manometer, .492; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 2.2. Time of setting up cell, 12.30 P.M., March 8, 1909.

Time.	Temperature.		Volume N_2 .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
March 9.						
10.00 A.M.	0°.0	0°.1	89.23	2.462	2.227	.998
2.00 P.M.	0°.0	0°.1	89.37	2.461	"	.994
5.00 P.M.	0°.0	0°.2	89.46	2.460	"	.992
March 10.						
12.30 P.M.	0°.0	0°.3	90.06	2.456	"	.982
Mean,				2.460	2.227	

Molecular osmotic pressure, 24.60.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.105.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 12.7; (2) at conclusion of expr., 12.7; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, K_8 . Resistance of membrane, 226,000. *Corrections*: (1) liquids in manometer, .422; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 2.3. Time of setting up cell, 3 P.M., March 29, 1909.

Time.	Temperature.		Volume N_2 .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
March 30.						
10.00 A.M.	0°.0	0°.1	136.85	2.465	2.227	.988
5.00 P.M.	0°.0	0°.1	136.86	2.465	"	.988
10.00 P.M.	0°.0	0°.1	136.90	2.460	"	.992
March 31.						
10.00 A.M.	0°.0	0°.1	136.89	2.454	"	.997
Mean,				2.461	2.227	

Molecular osmotic pressure, 24.61.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.105.

Table III.

0.1 Wt. normal solution. Exp. No. 3. *Rotation*: (1) original, 12.70; (2) at conclusion of expr., 12.70; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, K_s. Resistance of membrane, 224,000. *Corrections*: (1) liquids in manometer, .419; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 2.0. Time of setting up cell, 12 noon, April 12, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 13.						
10.00 A.M.	0° .0	0° .2	136.03	2,466	2.227	1.002
2.00 P.M.	0° .0	0° .1	136.28	2,464	"	.998
5.00 P.M.	0° .0	0° .3	136.34	2,465	"	.996
April 14.						
2.00 P.M.	0° .0	0° .3	136.63	2,456	"	.998
Mean,				2.463	2.227	

Molecular osmotic pressure, 24.63.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.106.

Table IV.

0.1 Wt. normal solution. Exp. No. 4. *Rotation*: (1) original, 12.65; (2) at conclusion of expr., 12.65; loss, 0 per cent. *Manometer*: No. 11; volume of nitrogen, 431.37. Cell used, Q_s. Resistance of membrane, 373,000. *Corrections*: (1) liquids in manometer, .413; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 2.1. Time of setting up cell, 2.30 P.M., March 24, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
March 24.						
10.00 P.M.	0° .0	0° .1	143.16	2.463	2.227	.983
March 25.						
9.30 A.M.	0° .0	0° .3	144.32	2.460	"	.960
2.00 P.M.	0° .0	0° .3	144.53	2.448	"	.968
10.00 P.M.	0° .0	0° .1	144.43	2.443	"	.975
Mean,				2.454	2.227	

Molecular osmotic pressure, 24.54.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.102.

Table V.

0.2 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 24.90; (2) at conclusion of expr., 24.90; loss, 0=0 per cent. *Manometer*: No. 5; volume of nitrogen, 637.60. Cell used, Z_s . Resistance of membrane, 290,000. *Corrections*: (1) liquids in manometer, .515; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 4.6. Time of setting up cell, 3 P.M., April 5, 1909.

Time.	Temperature.		Volume N_2 .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 6.						
10.00 A.M.	0° 0	0° 3	122.96	4.721	4.453	.999
2.00 P.M.	0° 0	0° 2	123.01	4.722	"	.996
5.00 P.M.	0° 0	0° 2	123.08	4.718	"	.997
April 7.						
11.00 A.M.	0° 0	0° 4	123.20	4.719	"	.990
Mean,				4.720	4.453	

Molecular osmotic pressure, 23.60.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.060.

Table VI.

0.2 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 24.90; (2) at conclusion of expr., 24.90; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, K_s . Resistance of membrane, 193,000. *Corrections*: (1) liquids in manometer, .495; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 4.5. Time of setting up cell, 3 P.M., April 5, 1909.

Time.	Temperature.		Volume N_2 .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 6.						
11.00 A.M.	0° 0	0° 3	79.29	4.712	4.453	.999
5.00 P.M.	0° 0	0° 2	79.27	4.715	"	.997
10.00 P.M.	0° 0	0° 3	79.24	4.720	"	.994
April 7.						
12.00 Noon	0° 0	0° 2	79.30	4.720	"	.990
Mean,				4.717	4.453	

Molecular osmotic pressure, 23.585.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.059.

Table VII.

0.2 Wt. normal solution. Exp. No. 3. *Rotation*: (1) original, 24.9; (2) at conclusion of expr., 24.9; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, Q₃. Resistance of membrane, 220,000. *Corrections*: (1) liquids in manometer, .495; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 4.7. Time of setting up cell, 4 P.M., April 14, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 15.						
10.00 A.M.	0°.0	0°.2	78.82	4.738	4.453	1.004
2.00 P.M.	0°.0	0°.2	78.85	4.737	"	1.003
9.30 P.M.	0°.0	0°.2	78.94	4.727	"	1.007
10.00 A.M.	0°.0	0°.4	78.93	4.725	"	1.010
Mean,				4.732	4.453	

Molecular osmotic pressure, 23.66.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.062.

Table VIII.

0.2 Wt. normal solution. Exp. No. 4. *Rotation*: (1) original, 24.90; (2) at conclusion of expr., 24.90; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, M₃. Resistance of membrane, 277,500. *Corrections*: (1) liquids in manometer, .495; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 4.6. Time of setting up cell, 4 P.M., April 16, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 17.						
10.30 A.M.	0°.0	0°.3	79.03	4.725	4.453	1.003
2.00 P.M.	0°.0	0°.3	79.04	4.727	"	1.000
April 18.						
11.30 A.M.	0°.0	0°.2	79.09	4.722	"	1.002
5.00 P.M.	0°.0	0°.2	79.10	4.727	"	.997
Mean,				4.725	4.453	

Molecular osmotic pressure, 23.625.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.061.

Table IX.

0.3 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 36.60; (2) at conclusion of expr., 36.60; net loss, 0=0 per cent. *Manometer*: No. 11; volume of nitrogen, 431.37. Cell used, M_4 . Resistance of membrane, 224,000. *Corrections*: (1) liquids in manometer, .526; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 6.75. Time of setting up cell, 3 P.M., March 15, 1909.

Time.	Temperature.		Volume N_2 .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
March 16.						
10.00 A.M.	0° .0	0° .1	57.23	7.084	6.680	1.000
2.00 P.M.	0° .0	0° .1	57.28	7.083	"	.994
10.00 P.M.	0° .0	0° .1	57.31	7.082	"	.991
March 17.						
5.00 P.M.	0° .0	0° .1	57.34	7.073	"	.996
Mean,				7.081	6.680	

Molecular osmotic pressure, 23.603.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.060.

Table X.

0.3 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 36.60; (2) at conclusion of expr., 36.60; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, M_3 . Resistance of membrane, 185,000. *Corrections*: (1) liquids in manometer, .530; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 7.04. Time of setting up cell, 3 P.M., April 20, 1909.

Time.	Temperature.		Volume N_2 .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 21.						
2.00 P.M.	0° .0	0° .1	54.89	7.062	6.680	.994
5.00 P.M.	0° .0	0° .1	54.86	7.067	"	.993
April 22.						
10.00 A.M.	0° .0	0° .1	54.83	7.073	"	.991
2.00 P.M.	0° .0	0° .1	54.83	7.074	"	.990
Mean,				7.069	6.680	

Molecular osmotic pressure, 23.563.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.058.

Table XI.

0.4 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 47.85; (2) at conclusion of expr., 47.85; loss, 0=0 per cent. *Manometer*: No. 13; volume of nitrogen, 263.04. Cell used, D₃. Resistance of membrane, 236,000. *Corrections*: (1) liquids in manometer, .573; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 9.51. Time of setting up cell, 12 Noon, February 2, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
Feb. 3.						
9.00 A.M.	0°.0	0°.1	26.63	9.472	8.906	.999
5.00 P.M.	0°.0	0°.3	26.72	9.443	"	.994
9.30 P.M.	0°.0	0°.1	26.61	9.484	"	.994
Feb. 4.						
9.00 A.M.	0°.0	0°.1	26.67	9.462	"	.994
Mean,				9.465	8.906	

Molecular osmotic pressure, 23.663.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.063.

Table XII.

0.4 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 47.85; (2) at conclusion of expr., 47.85; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, E₃. Resistance of membrane, 183,000. *Corrections*: (1) liquids in manometer, .549; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 9.1. Time of setting up cell, 2 P.M., March 27, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
March 28.						
11.00 A.M.	0°.0	0°.1	41.88	9.425	8.906	.980
March 29.						
10.00 A.M.	0°.0	0°.2	41.81	9.434	"	.988
12.00 Noon	0°.0	0°.2	41.79	9.440	"	.987
3.00 P.M.	0°.0	0°.2	41.80	9.440	"	.985
Mean,				9.435	8.906	

Molecular osmotic pressure, 23.588.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.059.

Table XIII.

0.5 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 58.95; (2) at conclusion of expr., 58.95; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, E₃. Resistance of membrane, 140,000. *Corrections*: (1) liquids in manometer, .555; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 11.7. Time of setting up cell, 3 P.M., April 9, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 10.						
1.00 P.M.	0°.0	0°.1	33.52	11.862	11.133	1.006
5.00 P.M.	0°.0	0°.1	33.49	11.870	"	1.008
April 11.						
5.00 P.M.	0°.0	0°.2	33.43	11.884	"	1.017
April 12.						
10.00 A.M.	0°.0	0°.1	33.37	11.912	"	1.010
Mean,				11.882	11.133	

Molecular osmotic pressure, 23.764.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.067.

Table XIV.

0.5 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 58.95; (2) at conclusion of expr., 58.95; loss, 0=0 per cent. *Manometer*: No. 11; volume of nitrogen, 431.37. Cell used, M₃. Resistance of membrane, 160,000. *Corrections*: (1) liquids in manometer, .559; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 11.8. Time of setting up cell, 3 P.M., April 9, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 10.						
1.00 P.M.	0°.0	0°.1	34.96	11.912	11.133	1.006
5.00 P.M.	0°.0	0°.1	34.89	11.935	"	1.008
April 11.						
11.00 A.M.	0°.0	0°.1	34.92	11.912	"	1.020
April 12.						
10.00 A.M.	0°.0	0°.1	35.01	11.890	"	1.010
Mean,				11.912	11.133	

Molecular osmotic pressure, 23.824.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.070.

Table XV.

0.6 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 69.3; (2) at conclusion of expr., 69.3; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, E₂. Resistance of membrane, 151,000. *Corrections*: (1) liquids in manometer, .564; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 14.02. Time of setting up cell, 3 P.M., March 18, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
March 19						
12.00 Noon	0° .0	0° .1	27.89	14.364	13.359	.993
5.00 P.M.	0° .0	0° .1	27.88	14.367	"	.995
March 20.						
2.00 P.M.	0° .0	0° .1	27.88	14.373	"	.990
5.00 P.M.	0° .0	0° .1	27.89	14.367	"	.990
Mean,				14.368	13.359	

Molecular osmotic pressure, 23.947.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.075.

Table XVI.

0.6 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 69.2; (2) at conclusion of expr., 69.2; loss, 0=0 per cent. *Manometer*: No. 11; volume of nitrogen, 431.37. Cell used, Q₂. Resistance of membrane, 212,000. *Corrections*: (1) liquids in manometer, .565; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 14.3. Time of setting up cell, 3 P.M., April 7, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
April 8.						
10.00 A.M.	0° .0	0° .1	29.11	14.400	13.359	1.004
5.00 P.M.	0° .0	0° .1	29.20	14.359	"	.999
April 9.						
10.00 A.M.	0° .0	0° .1	29.13	14.399	"	.995
2.00 P.M.	0° .0	0° .1	29.12	14.404	"	.995
Mean,				14.391	13.359	

Molecular osmotic pressure, 23.985.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.077.

Table XVII.

0.7 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 79.25; (2) at conclusion of expr., 79.25; loss, 0=0 per cent. *Manometer*: No. 5; volume of nitrogen, 637.60. Cell used, M₂. Resistance of membrane, 515,000. *Corrections*: (1) liquids in manometer, .629; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 16.8. Time of setting up cell, 2 P.M., February 13, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
Feb. 24.						
12.00 Noon	0°.0	0°.3	37.01	16.897	15.586	.980
9.30 P.M.	0°.0	0°.1	37.05	16.878	"	.982
Feb. 25.						
9.00 A.M.	0°.0	0°.1	37.05	16.866	"	.994
5.00 P.M.	0°.0	0°.4	37.03	16.871	"	.999
Mean,				16.878	15.586	

Molecular osmotic pressure, 24.111.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.083.

Table XVIII.

0.7 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original 79.30; (2) at conclusion of expr., 79.30; loss, 0=0 per cent. *Manometer*: No. 6; volume of nitrogen, 412.00. Cell used, D₂. Resistance of membrane, 280,000. *Corrections*: (1) liquids in manometer, .572; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 16.59. Time of setting up cell, 2.30 P.M., March 24, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
March 25.						
9.30 A.M.	0°.0	0°.3	23.86	16.897	15.586	.960
5.00 P.M.	0°.0	0°.3	23.83	16.907	"	.972
March 26.						
2.00 P.M.	0°.0	0°.1	23.79	16.925	"	.984
10.00 P.M.	0°.0	0°.2	23.83	16.892	"	.988
Mean,				16.905	15.586	

Molecular osmotic pressure, 24.150.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.085.

Table XIX.

0.8 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 89.00; (2) at conclusion of expr., 89.00; loss, 0=0 per cent. *Manometer*: No. 11; volume of nitrogen, 431.37. Cell used, D₃. Resistance of membrane, 550,000. *Corrections*: (1) liquids in manometer, .576; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 19.01. Time of setting up cell, 4 P.M., February 19, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
Feb. 20.						
11.00 P.M.	0° 0	0° 4	21.74	19.448	17.812	.992
Feb. 21.						
11.00 A.M.	0° 0	0° 0	21.68	19.495	"	.998
6.00 P.M.	0° 0	0° 0	21.71	19.470	"	.996
Feb. 22.						
9.00 A.M.	0° 0	0° 0	21.72	19.452	"	1.004
Mean,				19.466	17.812	

Molecular osmotic pressure, 24.333.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.093.

Table XX.

0.8 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 89.00; (2) at conclusion of expr., 89.00; loss, 0=0 per cent. *Manometer*: No. 5; volume of nitrogen, 637.60. Cell used, H₂. Resistance of membrane, 366,667. *Corrections*: (1) liquids in manometer, .636; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 19.1. Time of setting up cell, 4 P.M., February 19, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
Feb. 20.						
12.00 Noon	0° 0	0° 2	32.18	19.487	17.812	.985
11.00 P.M.	0° 0	0° 4	32.17	19.482	"	.992
Feb. 21.						
11.00 A.M.	0° 0	0° 0	32.14	19.496	"	.998
Feb. 22.						
9.00 A.M.	0° 0	0° 0	32.16	19.478	"	1.004
Mean,				19.486	17.812	

Molecular osmotic pressure, 24.358.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.094.

Table XXI.

0.9 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 98.15; (2) at conclusion of expr., 98.15; loss, 0=0 per cent. *Manometer*: No. 11; volume of nitrogen, 431.37. Cell used, F₃. Resistance of membrane, 550,000. *Corrections*: (1) liquids in manometer, .580; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 21.45. Time of setting up cell, 3 P.M., February 17, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
Feb. 18.						
8.30 A.M.	0° 0	0° 1	19.11	22.163	20.039	1.007
5.00 P.M.	0° 0	0° 2	19.12	22.162	"	1.004
Feb. 19.						
9.00 A.M.	0° 0	0° 4	19.14	22.130	"	0.994
12.00 Noon	0° 0	0° 2	19.15	22.140	"	0.990
Mean,				22.149	20.039	

Molecular osmotic pressure, 24.610.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.105.

Table XXII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 98.10; (2) at conclusion of expr., 98.10; loss, 0=0 per cent. *Manometer*: No. 5; volume of nitrogen, 637.60. Cell used, D₃. Resistance of membrane, 160,000. *Corrections*: (1) liquids in manometer, .640; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 21.78. Time of setting up cell, 2.30 P.M., March 11, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
March 12.						
10.00 A.M.	0° 0	0° 1	28.43	22.075	20.039	1.012
12.00 Noon	0° 0	0° 1	28.43	22.079	"	1.008
10.00 P.M.	0° 0	0° 1	28.40	22.106	"	1.005
March 13.						
12.00 Noon	0° 0	0° 2	28.44	22.086	"	.994
Mean,				22.087	20.039	

Molecular osmotic pressure, 24.541.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.102.

Table XXIII.

1.0 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 107.4; (2) at conclusion of expr., 107.4; loss, 0=0 per cent. *Manometer*: No. 20; volume of nitrogen, 411.13. Cell used, D₃. Resistance of membrane, 1,080,000. *Corrections*: (1) liquids in manometer, .591; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 24.35. Time of setting up cell, 4 P.M., January 20, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
Jan. 21.						
9.00 P.M.	0°.0	0°.1	16.26	24.883	22.265	1.006
Jan. 22.						
12.00 Noon	0°.0	0°.4	16.28	24.864	"	1.007
5.00 P.M.	0°.0	0°.5	16.26	24.891	"	1.005
Jan. 23.						
9.00 A.M.	0°.0	0°.2	16.28	24.864	"	1.004
Mean,				24.878	22.265	

Molecular osmotic pressure, 24.878.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.117.

Table XXIV.

1.0 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 107.4; (2) at conclusion of expr., 107.4; loss, 0=0 per cent. *Manometer*: No. 11; volume of nitrogen, 431.37. Cell used, D₃. Resistance of membrane, 550,000. *Corrections*: (1) liquids in manometer, .580; (2) dilution, 0; (3) concentration, 0; (4) capillary depression, .02. Initial pressure, 24.6. Time of setting up cell, 3.30 P.M., February 13, 1909.

Time.	Temperature.		Volume N ₂ .	Pressure.		Barometric Pressure.
	Solution.	Manometer.		Osmotic.	Gas.	
Feb. 14.						
11.00 A.M.	0°.0	0°.3	17.14	24.760	22.265	1.006
Feb. 15.						
1.00 P.M.	0°.0	0°.3	17.12	24.798	"	.997
5.00 P.M.	0°.0	0°.3	17.13	24.783	"	.997
11.30 P.M.	0°.0	0°.3	17.12	24.801	"	.994
Mean,				24.786	22.265	

Molecular osmotic pressure, 24.786.

Molecular gas pressure, 22.265.

Ratio of osmotic to gas pressure, 1.113.

Table XXV.—Summary of Results.

Weight normal concentration.	Osmotic pressure.	Gas pressure.	Difference	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure
0.1	2.460	2.227	.233	24.60	22.265	1.105
"	2.461	"	.234	24.61	"	1.105
"	2.463	"	.236	24.63	"	1.106
"	2.454	"	.227	24.54	"	1.102
0.2	4.720	4.453	.267	23.600	"	1.060
"	4.717	"	.264	23.585	"	1.059
"	4.732	"	.279	23.660	"	1.062
"	4.725	"	.272	23.625	"	1.061
0.3	7.081	6.680	.401	23.603	"	1.060
"	7.069	"	.389	23.563	"	1.058
0.4	9.465	8.906	.559	23.663	"	1.063
"	9.435	"	.529	23.588	"	1.059
"	11.882	11.113	.749	23.764	"	1.067
0.5	11.912	"	.779	23.824	"	1.070
0.6	14.368	13.359	1.009	23.947	"	1.075
"	14.391	"	1.032	23.985	"	1.077
0.7	16.878	15.586	1.292	24.111	"	1.083
"	16.905	"	1.319	24.150	"	1.085
0.8	19.466	17.812	1.654	24.333	"	1.093
"	19.486	"	1.674	24.358	"	1.094
0.9	22.149	20.039	2.109	24.610	"	1.105
"	22.087	"	2.048	24.541	"	1.102
1.0	24.878	22.265	2.613	24.878	"	1.117
"	24.786	"	2.521	24.786	"	1.113

Table XXVI.—Summary of Results. Mean Values.

Weight normal concentration.	Osmotic pressure.	Gas pressure.	Difference	Molecular osmotic pressure.	Molecular gas pressure	Ratio of osmotic to gas pressure.
0.1	2.460	2.227	.233	24.600	22.265	1.105
0.2	4.724	4.453	.271	23.620	"	1.061
0.3	7.075	6.680	.395	23.583	"	1.059
0.4	9.450	8.906	.544	23.625	"	1.061
0.5	11.897	11.133	.764	23.794	"	1.069
0.6	14.380	13.359	1.021	23.967	"	1.076
0.7	16.892	15.586	1.306	24.131	"	1.084
0.8	19.476	17.812	1.664	24.345	"	1.094
0.9	22.118	20.039	2.079	24.576	"	1.104
1.0	24.832	22.265	2.567	24.832	"	1.115

Discussion.

On examining the results one can readily see that the osmotic pressures obtained are somewhat higher than in previous work at 0° . This is believed to be due to the fact that now the work in this laboratory has reached such a stage that the great difficulty due to dilution has been overcome. In order to determine if dilution has taken place, the rotation of the sugar solutions at beginning and at end of each experiment was determined in order to ascertain if final rotation is less than initial rotation. Since the more dilute the solution the smaller the rotations, then any loss in rotation which may be found is due to the solution having become diluted in some way or another. Throughout this series at 0° in no successful experiment was there any loss in rotation. A few experiments which turned out to be failures did show a loss in rotation, but this was found to be due to the fact that a new cell had been used whose membrane was not strong and dense enough to be really semipermeable. In all experiments the observed pressures must remain constant for at least twenty-four hours, but when the cells are new the maximum pressure is reached within a very few hours, but remains there only for a short time, when, if the membrane is still too weak, the pressure begins to fall off and the solution when removed from the cell shows loss in rotation.

This series at 0° exhibits from weight-normal to 0.3 weight-normal the gradual falling off in value of the ratios of osmotic to gas pressure as has been observed in osmotic pressure determinations at higher temperatures. From 0.3 to 0.1 weight normal these ratios, as in all the other work on cane sugar, increase. On examining the 0.1 concentration, however, it will be seen that the difference between the ratio at 0.2 and 0.1 weight normal is much greater than the difference between the ratios at any other two consecutive concentrations. As table XXV indicates, a number of experiments were made in this region to determine as accurately as possible the pressures at these concentrations. Unfortunately, a greater number of experiments could not be made, but the results of

the four determinations at both concentrations were obtained by using different cells and different manometers, and since they are in rather close agreement it is thought that this great difference in the ratios of the two concentrations is genuine. Several other determinations of the 0.1 concentration were tried, but had to be made with new cells, whose membranes were insufficiently developed; but even in these cases the ratio of osmotic to gas pressure was much greater than had been expected. It is notable that this peculiarity in the osmotic pressure of the 0.1 concentrations appears where the temperature of the measurement of osmotic pressure is close to the freezing point of the solution. The difference between them being only $0^{\circ}.195$. Additional work will be done on these two concentrations, especially on concentrations between 0.1 N and 0.2 N to determine if there is a gradual rise in the value of the ratios from 0.2 N to 0.1 N. Before this work has been done it would be futile to attempt to assign any explanation for this peculiarity.

Barometer Effect.

During this work on the 0.1 N solutions, a new difficulty in direct measurements of osmotic pressures made itself felt. As will be brought out further on in this dissertation, the accuracy with which such measurements can now be made for all temperatures thus far worked with is far greater than at any previous time.

In the previous work, correction was made for the barometric pressure, but since the work was not as accurate as now the variation in the magnitude of this correction did not influence the results very greatly and no anxiety was felt if the atmospheric pressure during any one experiment exhibited very wide fluctuations. This year, however, it was found that for low concentrations, variations in atmospheric pressure were a factor that had to be reckoned with and will in the future demand serious attention. For the higher concentrations, where the osmotic pressures are large, such variations have but little effect on the ratio of osmotic pressure to gas pressure, as can be seen from the results in Table XXV.

At 0.1 N concentrations a variation of 0.005 or 0.010 of an atmosphere calls for a variation in height of the mercury column in most of our manometers of 0.06 mm. and 0.12 mm., respectively, a change which can very easily be detected. Now, if the atmospheric pressure should at these low concentrations change an amount corresponding to above values, then the height of the mercury column should vary accordingly, but, unfortunately, the membranes of our cells do not respond to rapid changes and require several hours to adapt themselves to any variation. In the meantime the atmospheric pressure may again change, thus before the cell has adjusted itself to the first state of affairs a new condition of things has set in. As is evident, in order for the cell to reach the equilibrium just referred to, water must pass either through the membrane into the cell or out of cell, depending on whether atmospheric pressure is increasing or decreasing. In this respect the analogy of the barometer effects to the thermometer effects is a striking one.

Below are two tables which bring out this barometer effect. The data recorded is that of two experiments on 0.1 N concentrations. They were made with an old cell and with a new cell. In these tables all pressures are recorded in atmospheres. The total pressure corrected for barometric pressure gives the osmotic pressure. In both tables the recorded readings are consecutive.

Table XXVII.—0.1 N. New Cell.

Reading.	Barometric pressure.	Total pressure.	Osmotic pressure.
1	1.002	3.441	2.439
2	.998	3.437	2.439
3	.996	3.436	2.440
4	.994	3.432	2.438
5	.997	3.436	2.439

Table XXVII is the record of an experiment with a new cell, whose membrane was not as dense as that in an older cell, and in consequence water passed freely inward and outward through the membrane. This is shown by the fact that

the greatest deviation in total pressures is 0.009 of an atmosphere which is very nearly offset by a deviation of 0.008 of an atmosphere in barometric pressure, and as a result the osmotic pressures are practically constant.

Table XXVIII.—0.1 N. Old Cell.

Reading.	Barometric pressure.	Total pressure.	Osmotic pressure.
1	0.998	3.403	2.405
2	0.994	3.404	2.410
3	0.992	3.404	2.412
4	0.990	3.406	2.416
5	0.983	3.405	2.422
6	0.982	3.406	2.424
7	0.986	3.402	2.416
8	1.003	3.402	2.399

Table XXVIII shows the results for the same concentration as Table XXVII, but with an old cell, in which the membrane was much more dense. The first six readings show practically constant total pressures, whereas barometric pressure varied in these six readings 0.016 of an atmosphere; the osmotic pressure, on the other hand, shows a variation of 0.009 of an atmosphere. Since these readings cover a period of twenty-four hours, it can be seen that during this time the cell was making ineffectual attempts to follow the changing atmospheric pressure. Readings 7 and 8 bring out the barometer effect even more strikingly, for, although the total pressures remained constant, the barometric pressure varied 0.017 of an atmosphere, and as a result the osmotic pressure varied by the same amount. The interval between these two readings was four hours. For 0.1 N concentrations where the total osmotic pressure measured is only about 3.46 atmospheres this causes an error of .5%. In higher concentrations, of course, a variation of 0.017 of an atmosphere is almost negligible.

Regarding the results at higher concentrations very little need be said. One noticeable feature, however, is seen on examining the tabulation of these results in Table XXV. For

the concentrations from 0.5 N to 1.0 N one of the experiments shows a somewhat higher ratio than the other experiment. The manometers used in this work have been in use for several months, and it was thought necessary to check up their nitrogen volumes against our standard manometer, for it is known that the nitrogen volumes of the manometers undergo a slight change in value when in constant use. It is possible that in consequence of this restandardization the results will have to be slightly altered, but in no case would the correction be large.

An idea of the comparative accuracy with which the various concentrations can be measured will no doubt prove interesting. In the following table has been recorded for each concentration the greatest deviation in decimal parts of an atmosphere, the maximum deviation from the mean and the percentage of greatest deviation from mean in terms of total pressure measured. The total pressure is, of course, the osmotic pressure plus the barometric pressure and is the pressure actually measured, and any errors of observation which may be made are made on this total pressure.

Table XXIX.—Table of Comparative Accuracy.

Concentration weight normal.	Greatest deviation.	Greatest deviation from mean.	%
0.1	0.009	0.006	0.17
0.2	.015	.008	.14
0.3	.012	.006	.07
0.4	.030	.015	.14
0.5	.030	.015	.12
0.6	.023	.012	.08
0.7	.027	.014	.08
0.8	.020	.010	.05
0.9	.062	.031	.13
1.0	.092	.046	.18

This table gives an idea as to which are the most difficult concentrations to work with, namely, the 0.1 and the 1.0 weight normal solutions.

Temperature Coefficient.

The results of this work at 0° when taken together with the results at 5° and 10° establish the important fact that the law of Gay Lussac holds for osmotic pressure of cane sugar solutions over the range of temperatures studied up to the present time. This is shown by the following tables, in the first of which is recorded the osmotic pressure for each concentration and in the second the ratio of osmotic to gas pressure.

Table XXX.—Osmotic Pressures in Atmospheres.

Weight normal concentration.	At 0°	At 5°	At 10°
0.1		2.452	2.497
0.2	4.724	4.819	4.895
0.3	7.075	7.201	
0.4	9.450	9.620	9.790
0.5	11.897	12.091	12.297
0.6	14.380	14.605	14.851
0.7	16.892	17.206	17.501
0.8	19.476	19.820	20.161
0.9	22.118	22.464	22.886
1.0	24.832	25.289	25.697
Total osmotic pressure from			
0.4-1.0	119.045	121.095	123.183
Difference	2.050	2.088	
Difference per degree..	.410	.418	

Owing to the fact that at 0° more work will have to be done to show more exactly what the osmotic pressure for the 0.1 N should be, and since at 10° time did not permit a determination of the osmotic pressure of the 0.3 N, the total osmotic pressure recorded in above table covers only the concentrations from 0.4 N to 1.0 N. This, however, is a sufficient number to show that as temperature increases the osmotic pressure increases, and that it increases by an amount which is in fairly close agreement with that demanded by the law of Gay Lussac.

Table XXXI.—Mean ratios of Osmotic to Gas Pressure.

Weight normal concentration.	0°	5°	10°
0.1	1.105	1.082	1.082
0.2	1.061	1.063	1.061
0.3	1.059	1.059	
0.4	1.061	1.061	1.061
0.5	1.069	1.067	1.066
0.6	1.076	1.074	1.072
0.7	1.084	1.084	1.083
0.8	1.094	1.093	1.092
0.9	1.104	1.101	1.102
1.0	1.115	1.115	1.114

Table XXXI brings out the temperature coefficient in another manner. If osmotic pressure obeys the law of Gay Lussac, then the ratio of osmotic pressure to the theoretical gas pressure should remain constant for all three temperatures. As the table indicates, for all concentrations, except the .01 N at 0°, the ratios for the three temperatures agree closely, the difference being confined to the third decimal place. Why the ratio of the 0.1 N at 0° should not agree with the ratio of the 0.1 N at the higher temperatures is at present not known.

Biography.

Emanuel G. Zies was born in Baltimore, Md., September 26, 1883. He received his early education in the public schools of that city. In 1903 he entered the undergraduate department of the Johns Hopkins University and received the degree of A. B. in 1906. In the fall of 1906 he entered the graduate department of the same university, making chemistry his principal subject; physical chemistry and applied geology were his first and second subordinates, respectively.

In 1907-1908 he held a University scholarship and in 1908-1909 he held a fellowship.

